Regular Article

Leaf-like hybrid of bismuth subcarbonate nanotubes/graphene sheet with highly efficient photocatalytic activities

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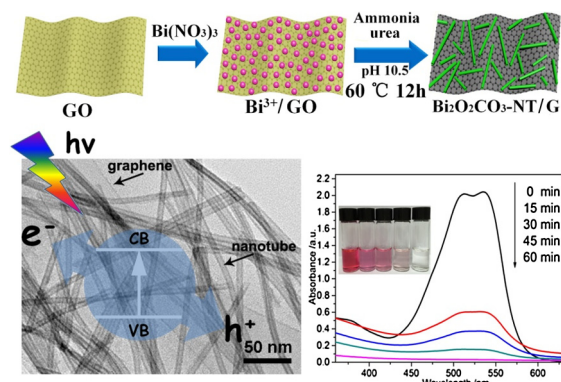
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GRAPHICAL ABSTRACT

In this work, leaf-like hybrid with $Bi_2O_2CO_3$ nanotubes as the "veins" and graphene sheet as the "laminae" is fabricated via a facile one-pot reaction of bismuth nitrate and graphene oxide in alkaline aqueous solution. With the uniform distribution of $Bi_2O_2CO_3$ nanotubes on the graphene substrate, the obtained $Bi_2O_2CO_3$-NT/G manifests high specific surface area (90.4 $m^2\,g^{-1}$) and large pore volume (0.197 $cm^3\,g^{-1}$), which are favorable for the efficient light capturing and the rapid transfer of mass and charge carriers. In comparison with the pure $Bi_2O_2CO_3$ nanotubes and commercial $Bi_2O_2CO_3$, $Bi_2O_2CO_3$-NT/G exhibits much enhanced activity and long-term stability towards the photocatalytic degradation of organic compound X-3B, which is owing to its unique leaf-like structural features.

ARTICLE INFO

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1. Introduction

As a simple and low-cost technique, photodegradation with semiconductor as catalyst has been regarded as one of the most promising approaches to handle diversified organic contaminants in both air and water [1]. Generally, the heterogeneous photocatalysis process involves the generation, separation and migration of light-excited charge carriers followed by their redox reactions with the adsorbed substrates, which mainly take place on the surface of the semiconductors [1,2]. The degradation rate of organic contaminants is primarily related to the amount of active sites on the photocatalysts, which critically depends on the composition, crystallinity, morphology and surface area. Therefore, the delicate control over the microstructures of the catalysts, which means the fabrication of them into different nanostructures such as nanoparticles [3,4], nanofibers [5,6], nanosheets [7–9], nanaotubes [10–12] and even more complicated hierarchical architectures [13–16], provides opportunities to effectively promote their photocatalytic activities.

As a high performance photocatalyst, bismuth subcarbonate ($Bi_2O_2CO_3$) has gained intensive research interests since it possesses lamellar structures with CO_3^{2-} sandwiched between $(Bi_2O_2)^{2+}$ layers and a narrow band gap of 3.1–3.5 eV [12,14,16–19]. Similar to the other semiconductor photocatalysts, the performance of $Bi_2O_2CO_3$ is mainly limited by its fast charge recombination [1]. To improve the photocatalytic efficiency of $Bi_2O_2CO_3$, one strategy is to combine it with carbon nanomaterials, which can serve as the matrices to enhance the transfer of charge carriers [20–23]. With this respect, graphene with extended π-conjugated frameworks and unique two-dimensional (2D) morphology has been considered as an appealing candidate to enhance the separation efficiency of light-excited charge carriers in photocatalysts [20]. Liu et al. has prepared the hybrid of flower-like $Bi_2O_2CO_3$ and graphene with much better photocatalytic performance than $Bi_2O_2CO_3$ alone towards the degradation of Rhodamine B under visible light [24]. In another case, Zhang et al. found that the graphene-wrapped $Bi_2O_2CO_3$ manifested an enhanced photocatalytic behavior on the degradation of carbamazepine [25]. However, the $Bi_2O_2CO_3$ catalysts prepared in the above work usually have spherical or sheet-like structures with the diameters of 1–3 μm. Such morphologies with large sizes cannot ensure the efficient contacts between $Bi_2O_2CO_3$ and graphene, inevitably reducing their photoactivities [24,25]. Thus, the construction of graphene based $Bi_2O_2CO_3$ hybrids with conscientiously designed hierarchical structures and promoted photocatalytic activities is still highly challenging.

In this work, we have developed a facile approach towards leaf-like hybrid with highly crystallized $Bi_2O_2CO_3$ nanotubes (outer diameter ∼ 6.5 nm, and inner diameter ∼ 4 nm) as the "veins" and graphene sheets as the "laminae" via the one-pot reaction of bismuth nitrate ($Bi(NO_3)_3$) and graphene oxide (GO) in alkaline aqueous solution. Named as $Bi_2O_2CO_3$-NT/G, the hybrid manfests high specific surface area (90.4 m^2 g^{-1}) and large pore volume (0.197 cm^3 g^{-1}), which are favorable for the efficient light capturing and mass/charge transfer. With the unique leaf-like architecture, $Bi_2O_2CO_3$-NT/G displays much higher photocatalytic degradation behavior towards organic contaminant than the $Bi_2O_2CO_3$ nanotube and commercial $Bi_2O_2CO_3$.

2. Experimental section

2.1. Materials

Graphite powder, sulfuric acid (H_2SO_4, 98%), potassium permanagnate ($KMnO_4$, 99.5%), hydrogen peroxide (H_2O_2, 30%), sodium nitrate ($NaNO_3$, 99%), Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 99%), ammonia solution ($NH_3 \cdot H_2O$, 25–28%) and urea (CON_2H_4, 99%)were purchased from Sinopharm. hydrazine hydrate ($N_2H_4 \cdot H_2O$, >98%) was purchased from Aladdin All chemicals were of analytical degrees and used as received without further purification. Ultra-pure water was used throughout the experiment.

2.2. Synthesis of the samples

A homogeneous aqueous dispersion of GO (3.0 mg mL^{-1}) was first prepared from natural graphite flakes with the modified Hummers' method. The GO dispersion (5 mL) and $Bi(NO_3)_3 \cdot 5H_2O$ (400 mg in 5 mL HNO$_3$) were then mixed in deionized water (100 mL) and magnetically stirred for 0.5 h at room temperature. After adjusting the pH value of the mixture to ∼ 10.5 with ammonia solution, hydrazine hydrate (100 μL) [26] and urea (50 mg) were added, and the resulting suspension was magnetically stirred at 60 °C for 12 h. Finally, $Bi_2O_2CO_3$-NT/G was collected as grey precipitate, washed several times with DI water, and dried at 50 °C in the air.

In controlled experiments, $Bi(NO_3)_3 \cdot 5H_2O$ (400 mg) dissolved in HNO$_3$ (5 mL) was first added to deionized water (100 mL) and the pH value of the solution was adjusted the to ∼ 10.5 with ammonia. Subsequently, urea (50 mg) was added and the resulting mixture was magnetically stirred at 60 °C for 12 h. The resulting sample, named as $Bi_2O_2CO_3$-NT, was collected as white precipitate, washed several times with DI water, and dried at 50 °C in the air.

To prepare reduced graphene oxide (rGO), the aqueous dispersion GO (5 mL) was diluted in deionized water (100 mL). Hydrazine hydrate (100 μL) was added and the mixture was reacted at 95 °C for 1 h [27]. The precipitated rGO was collected, washed several times with DI water, and dried at 50 °C in the air.

2.3. Characterizations

Scanning electron microscopy (SEM) images were acquired using NOVA NanoSEM 230 (FEI, USA) microscope with an accelerating voltage of 5 kV. Transition electron microscopy (TEM) images were conducted using JEM-2100 (JEOL Ltd., Japan) microscope operating at 200 kV. X-ray diffraction (XRD) measurements were carried out on a X-ray diffractometer (D/max-2200/PC, Rigaku Corporation, Japan) using Cu Kα radiation (λ = 0.1542 nm) operated at 40 kV and 40 mA and at a scan rate of 5° per second. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using Spectrum 100 (Perkin Elmer, Inc., USA) spectrometer. The surface areas of the dried samples were analyzed in a nitrogen adsorption apparatus (ASAP 2010 M+C, Micromeritics Inc., USA). UV/Vis adsorption spectra were acquired with a spectrophotometer (Lambda 750S, Perkin Elmer, Inc, USA) equipped with an integrating sphere attachment. Photoluminescence measurements were performed at room temperature on a fluorescence spectrophotometer (LS 50B, Perkin Elmer, Inc., USA) using a Xenon discharge lamp as the excitation light source, and the excited wavelength was 250 nm.

2.4. Photodegradation measurements

The catalyst (40 mg) was dispersed in the aqueous solution of X-3B (50 mL, 150 ppm) in a cylindrical quartz vessel at room temperature in the air under 254 nm irradiation (PHILIPS, TUV11 W). Prior to illumination, the suspension was sonicated for 5 min and stirred for 30 min in the dark to reach the adsorption-desorption equilibrium. At 15 min intervals, the sample (5 mL) was withdrawn from the suspension and the corresponding concentration of X-3B was calculated by recording the absorbance at the